Computationally Designed Oligomers for High Contrast Black Electrochromic Polymers

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14. ABSTRACT
The goal of this proposed effort is to use theoretical calculations to identy electrochromic materials that can be switched between 100% transmissive and tinted black states. This work was carried out as an active collaboration with the synthetic effort of the Reynolds group at Georgia Tech. We formed a tight feedback loop between our two groups, such that the computational effort narrowed down the promising oligomers which were then synthesized and characterized, then fed back to our group for continuous benchmarking. At the onset of our project, we were seeking CMY chromophores which when combined wold give rise to a neraly black neutral state. Additionally, upon oxidation these polymers would have litte to no tailing form the near IR thereby guaranteeing nearly a 100% transmissive material. These systems were given the title of cathodically coloring materials. After a set of structural experiments were performed a new type of system was found where we had a nearly transmissive neutral state and a black oxidized state (anodically coloring materials). In all cases, we utilized a set of DFT/TDDFT treatments to produce insight of the impact structure-property relationships have on UV-Vis spectra.

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**COMPUTATIONALLY DESIGNED OLIGOMERS FOR
HIGH CONSTRAST BLACK ELECTROCHROMIC POLYMERS**

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I. Statement of Objectives

The goal of this proposed effort is to use theoretical calculations to identify electrochromic materials that can be switched between 100% transmissive and tinted black states. This work was carried out as an active collaboration with the synthetic effort of the Reynolds group at Georgia Tech. We formed a tight feedback loop between our two groups, such that the computational effort narrowed down the promising oligomers which were then synthesized and characterized, then fed back to our group for continuous benchmarking. At the onset of our project, we were seeking CMY chromophores which when combined would give rise to a nearly black neutral state. Additionally, upon oxidation these polymers would have little to no tailing from the near IR thereby guaranteeing nearly a 100% transmissive material. These systems were given the title of cathodically coloring materials. After a set of structural experiments were performed a new type of system was found where we had a nearly transmissive neutral state and black oxidized state (anodically coloring materials). In all cases, we utilized a set of DFT/TDDFT treatments to produce insight of the impact structure-property relationships have on UV-Vis spectra. Our overall objective is to capitalize on our results to provide the Reynolds group with a set of oligomers that will produce the desired transmissive/black states.

II. Accomplishment Overview.

In the last 18 months, we have successfully benchmarked our DFT computations to experiment such that we trust our simulations to strongly correlate to experimental UV/Vis. Additionally, we have performed hundreds of DFT/TDDFT computations on a variety of oligomers to gain insight into structure property relationships. In particular, we examined the impact of increasing conjugation as well as acceptor identity for our cathodically coloring systems which are comprised of donor-acceptor-donor (DAD). Our findings suggest that a conjugation length increase leads to an increase in spectral intensity as well as a red shift in the UV-Vis. The identity of the acceptor was found to have a strong impact on the neutral species but no impact what-so-ever on the bipolaron with respect to both the color and the UV-Vis spectrum. Apart from cathodically coloring compounds we also studied anodically coloring (all donor) materials. These oligomers demonstrated the same trends as were found in DAD systems with a red shift and an intensity increase upon incorporation of a longer conjugation length. Our most interesting finding was that steric strain incorporation caused the spectrum of the neutral species to be blue-shifted almost completely into the UV. Using this idea, the Reynolds group generated a polymer and from their measurements produced a material that was black upon oxidation but slightly yellow in the neutral state. Finally, we examined how well DFT/TDDFT can predict color and have shown that it is not able to do so with acceptable accuracy.

III. Specific Task Accomplishments

III.1 Benchmarking

In our first year we identified the best functional/basis set combination which produced the closest agreement to the Reynolds group experimental measurements. We began with the B3LYP (Becke, three-parameter, Lee-Yang-Parr)[1] hybrid functional which has been shown to produce

comparable geometries to Moller-Plesset second-order perturbation theory (a higher level of theory)[2] at a fraction of the computational cost.[3] This functional coupled with a 6-31G* basis set is known to be quite successful for many different systems.[4-10] After we examined the B3LYP/6-31G* pairing we tested other hybrid functional/basis set combinations against the available experimental results. To achieve an even better agreement, we used the polarizable conductor calculation model (CPCM)[11,12] which applies a solvent field allowing for potential dispersion effects and polarization. For basis set identification the sets examined included the following: 6-31G(d)[13-15], 6-31G(d,p)[16,17], 6-311G(d,p)[18], SV[19], SVP[20], cc-PVDZ[21]. The set of functionals included: B3LYP[18,21,22], B3PW91[23], HSEh1PBE[24], PBEh1PBE[25], B972[26], B971[27], B98[21], mPW3PBE[14], mPW1PBE[14]. After analyzing the results of all of these pairings we found that the mPW1PBE/cc-PVDZ provided the best correlation. As shown in **Figure 1**, this pairing
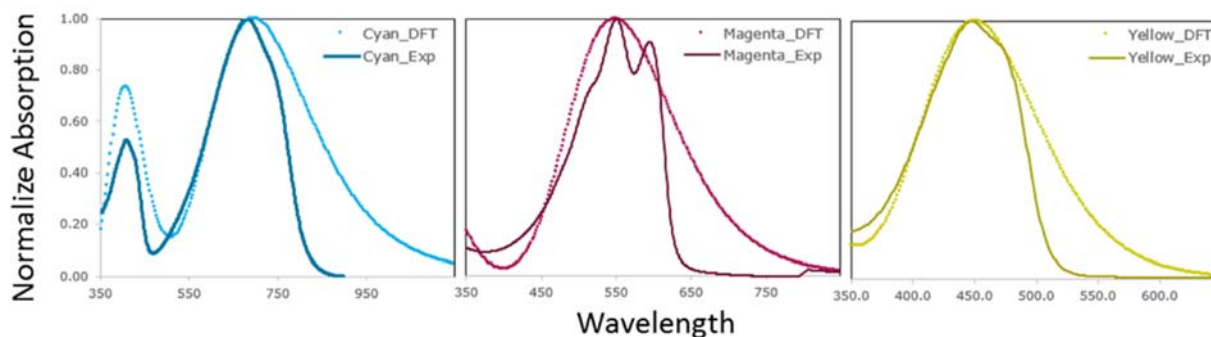
Figure 1: Absorbance spectra of cyan, magenta, and yellow theoretically treated oligomers (dotted line) and experimentally measured polymers (solid line), respectively.

produced theoretical absorption maxima which were very close to those found experimentally[28], thereby indicating that our treatment can reliably predict UV-Vis spectra.
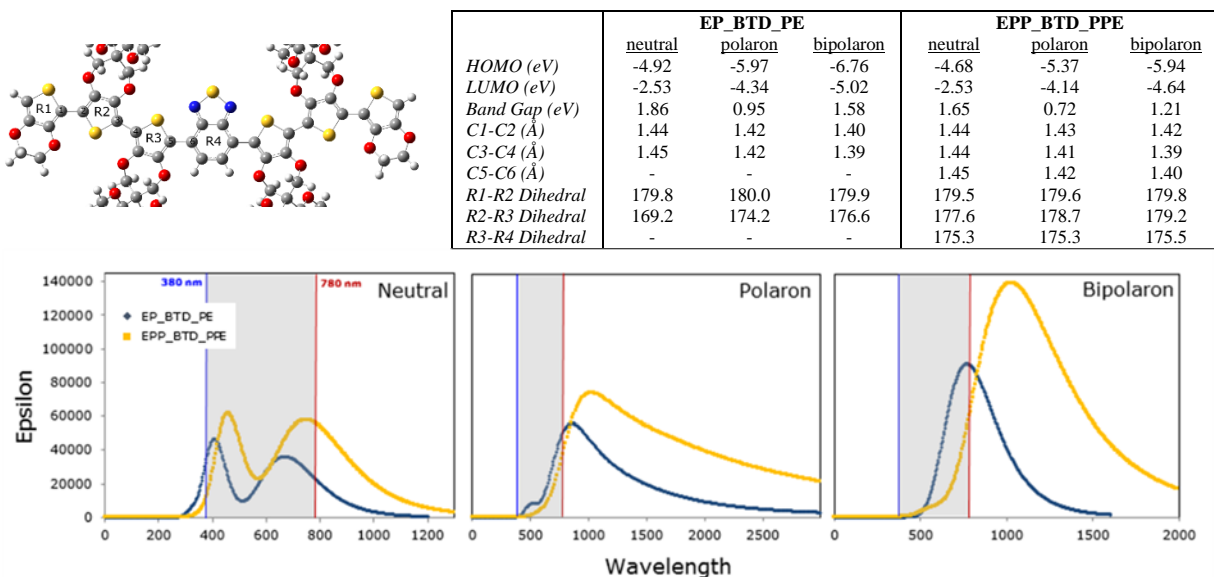
III.2 Structure-Property Oligomer Studies

In the original proposal we examined several different approaches in order to identify the best oligomers for the Reynolds group to formulate into devices. The one constant in all of these studies was to identify how structure impacted the geometry, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), frontier orbital diagrams, band gap and most importantly the predicted UV-Vis spectra.

III.2.1 Cathodically Colored Oligomers – Donor-Acceptor-Donor (DAD) Systems

Impact of Increased Conjugation: We began by examining the impact of increased conjugation by sandwiching BTD between 1 or 2 ProDOT (P) groups who were then terminated with ethylene dioxythiophene (EDOTs or E) as shown in **Figure 2**. Going from EP_BTD_PE to EPP_BTD_PPE led to a raising of the HOMO a lowering of the LUMO which then produced a smaller band gap. The geometry for both structures indicated that as charge was increased the backbone was more quinoidal in nature as evidenced by a reduction in the inter-ring carbon-carbon bond lengths. Additionally, the dihedrals between aryl rings became more planar upon oxidation. These two trends were proof that going from neutral to polaron and finally to bipolaron produced

a more planar oligomer. Finally, the UV-Vis of the more conjugated EPP_BTD_PPE was red-shifted and possessed higher intensity than the EP_BTD_PE. Overall, the main finding we made through this study was *increasing conjugation will reduce the impact of oxidation on planarization*.

	EP_BTD_PE			EPP_BTD_PPE		
	neutral	polaron	bipolaron	neutral	polaron	bipolaron
HOMO (eV)	-4.92	-5.97	-6.76	-4.68	-5.37	-5.94
LUMO (eV)	-2.53	-4.34	-5.02	-2.53	-4.14	-4.64
Band Gap (eV)	1.86	0.95	1.58	1.65	0.72	1.21
C1-C2 (Å)	1.44	1.42	1.40	1.44	1.43	1.42
C3-C4 (Å)	1.45	1.42	1.39	1.44	1.41	1.39
C5-C6 (Å)	-	-	-	1.45	1.42	1.40
R1-R2 Dihedral	179.8	180.0	179.9	179.5	179.6	179.8
R2-R3 Dihedral	169.2	174.2	176.6	177.6	178.7	179.2
R3-R4 Dihedral	-	-	-	175.3	175.3	175.5

Figure 2: A pictorial representation of the increased conjugation study. In the upper left is a diagram indicating the measurements which are given in the table in the upper right. The bottom portion represents the simulated UV-Vis spectra for the two systems with the left having a neutral charge, the middle having a cationic charge and finally the far right a dicationic charge. The grey area corresponds to the visible range which is sandwiched between 380 and 780 nm.

Impact of Acceptor Identity: For this set of structures, we compared BTD to denzooxadizole (BOD) and benzotriazole (BTz) all of which were sandwiched between ProDOT rings with terminating EDOT groups (EP_acceptor_PE). From the geometric results, it was determined that the BTD was much more twisted out of plane than the BOD and BTz oligomers. This trend indicated that *sterics plays a larger role than electron-withdrawing behaviors*. Another finding was that the same dication was produced regardless of the color or peak morphology of the neutral 5-heterocycle system (**Figure 3**). Hence, *acceptor identity has no impact on the dication that is produced.*
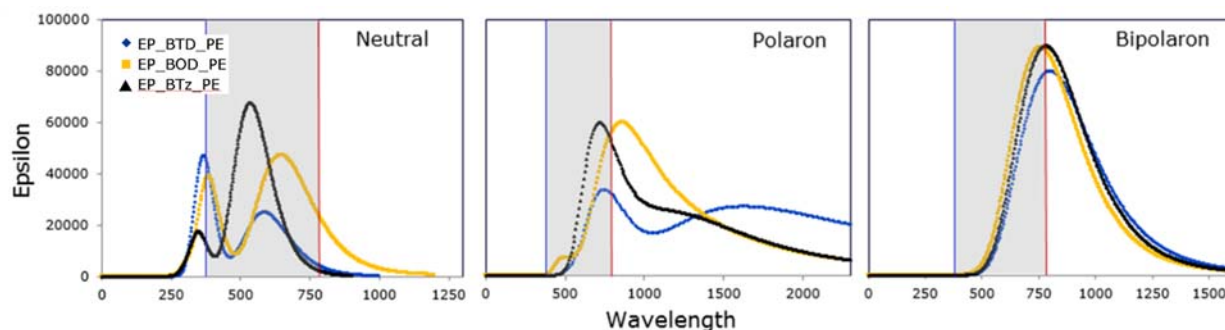
Figure 3: A pictorial representation of the UV-Vis spectra for the three systems possessing different acceptors with the left having a neutral charge, the middle having a cationic charge and finally the far right a dicationic charge. The grey area corresponds to the visible range which is sandwiched between 380 and 780 nm.

III.2.2 Anodically Colored Oligomers – All Donor Systems

Impact of Increased Conjugation: For this set of oligomers we again increased the number ProDOT aryl groups in which we started with a 3-heterocycle chromophore composed of EPE and ended with EPPPE. As was the case in the cathodically colored oligomers we found a raising in HOMO, a lowering of LUMO and a reduction in band gap when going from EPE to EPPPE. All three were virtually planar to begin with and remained so upon oxidation. Finally, the UV-Vis spectra again displayed a red-shifting and an intensity increase as ProDOTs were added to the oligomeric backbone.

Impact of Increased Steric Strain: Here we examined two sets of structures. Our first study involved replacing the P in EPE with acyclic dioxythiophene (AcDOT or A). The AcDOT 2-ethylhexyl side-chains caused a twist out of plane which led to a lowering of HOMO, raising of LUMO as well as an increase band gap. The geometry also indicated a large out of plane twist and EAE was greatly impacted by oxidation as near planarity was reached for the bipolaron. The EPE chromophore was already planar and so there was little to no change in planarity upon oxidation. The most interesting impact was found in the UV-Vis spectra. The added strain of the AcDOT forced the neutral geometry to blue-shift in which very little absorption occurred in the visible as shown in **Figure 4 b.**). Hence, *we can potentially use steric effects to obtain a transmissive neutral state*.
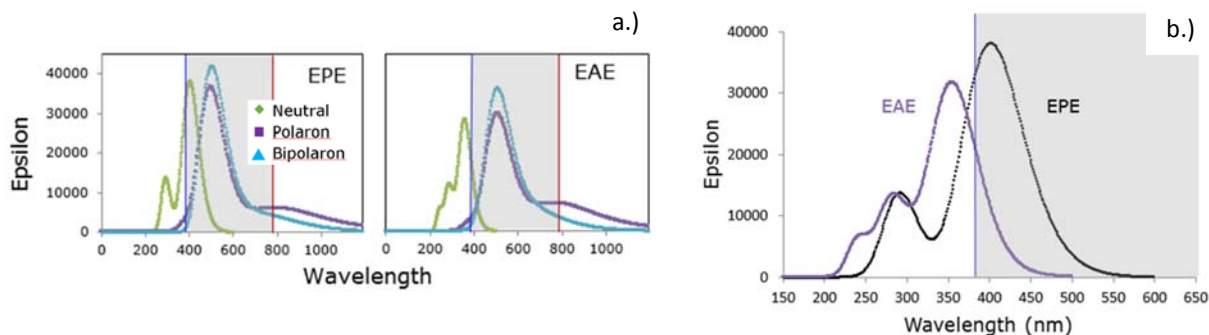
Figure 4: a.) The simulated UV-Vis spectra for the EPE and EAE in which the neutral (green), polaron (purple) and bipolaron (blue) is shown. b.) An enlargement of the neutral spectra is shown with EAE in purple and EPE in black. For both figures the grey area corresponds to the visible range which is sandwiched between 380 and 780 nm.

III.3 Anodically Coloring Yellow-Black Polymer

Impact of Increased Steric Strain & Increased Conjugation: We examined 4- and 5- heterocycle chromophores with more extensive conjugation, with the possibility of generating a much broader absorption peak in the visible as illustrated by the results of **Figure 5** and **Table 1**. Here, we incorporated not only Ac aryl groups but also included dimethoxybenzene (B) which gives rise to a large amount of strain in the backbone. As was previously the case, increased oxidation led to a quinoidal type structure for all species. The dihedral angle trends demonstrated a large amount of strain in EAcAcE indicative of a reduction in pi conjugation and an increase in band gap when compared to EAcE. On the other hand, EAcBAcE exhibited a reduction in band gap and thereby an increase in conjugation. These results are further supported by the UV-Vis spectra. Relative to EAcE, there was a hypsochromic shift for EAcAcE and a bathochromic shift for EAcBAcE in the neutral UV-Vis spectra shown in **Figure 5**. For the cationic spectra, the EAcBAcE species had a broad well-formed peak that was centered in the visible range. The EAcE was blue shifted and narrower while the EAcAcE was lies in between the others. This study lead us to examine more precisely exactly what is giving rise to the black color the Reynolds group found in their devices possessing EAcBAcE.
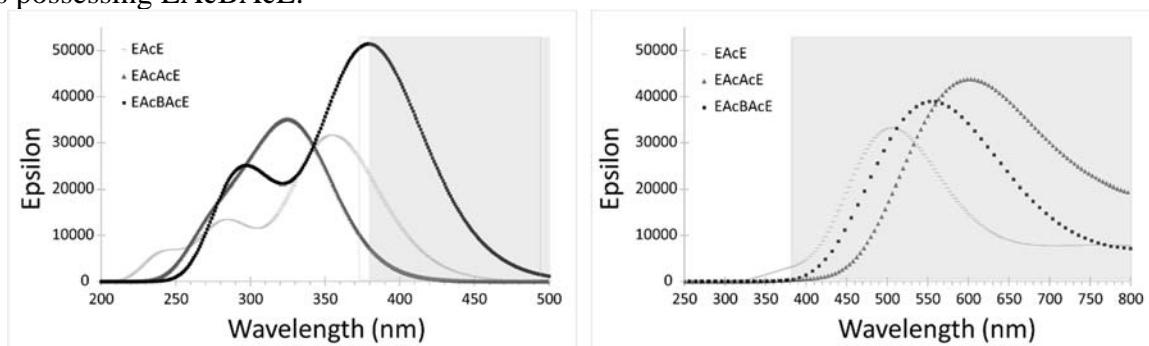
Figure 5. Neutral (left) and cationic (right) spectra of EAcE, EAcAcE, and EAcBAcE and their absorbance that occurs in the visible region (grey)

Dihedral measurements
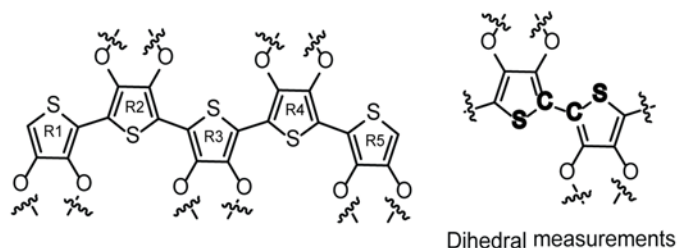
	EProE			EAcE			EAcAcE			EAcBAcE		
	neutral	cation	dication	neutral	cation	dication	neutral	cation	dication	neutral	cation	dication
Band Gap (eV)	3.09	-	-	3.49	-	-	3.74	-	-	3.26	-	-
R1-R2 (Å)	1.44	1.41	1.38	1.46	1.41	1.38	1.45	1.42	1.40	1.45	1.44	1.4
R2-R3 (Å)	1.44	1.41	1.38	1.44	1.41	1.36	1.45	1.40	1.38	1.47	1.45	1.41
R3-R4 (Å)	-	-	-	-	-	-	1.45	1.42	1.39	1.47	1.43	1.41
R4-R5 (Å)	-	-	-	-	-	-	-	-	-	1.44	1.41	1.41
R1-R2 Dihedral	179.4	180.0	180.0	55.4	163.5	167.2	53.2	163.0	178.3	49.4	43.6	179.4
R2-R3 Dihedral	179.4	180.0	180.0	174.0	179.4	177.1	53.3	175.8	164.2	125.6	150.8	158.9
R3-R4 Dihedral	-	-	-	-	-	-	57.0	173.8	178.9	125.9	155.6	173.9
R4-R5 Dihedral	-	-	-	-	-	-	-	-	-	173.3	178.5	167.8

Table 1: Structural data for all target oligomers in this study.

Charge State Elucidation of EAcBAcE: In the experimental spectroelectrochemistry for EAcBAcE, the charged state exhibited an unusually high-energy absorption characteristic compared to what was calculated. In order to shed some light into the unusual charge state absorption for EAcBAcE we went back to computational methods to look into the possible charge states that the chromophore could adopt. For this calculation, the chromophore is broken into pieces with the idea that the dimethoxybenzene would act as a steric block in the conjugation of the radical cation. **Figure 6** shows calculated radical cation state absorptions of segmented portions of the EAcBAcE chromophore overlaid with the experimental spectroelectrochemistry. These ***calculations suggest that there are in fact two radical cation states present in the chromophore upon oxidation***. The two-ring electron rich dioxythiophene portions of the chromophore (EAc) and/or the entire chromophore (EAcBAcE) are oxidized. This postulation is also corroborated by the fact that there is a large increase in absorption in this oxidized state, as a one transition material in the neutral can become two with both EAc portions oxidizing on one chromophore. Calculations do not indicate a contribution from the EAcB trimer, and this is likely due to the inter-ring steric strain in the Ac-B-Ac portion of the chromophore. Once the steric energy barrier is overcome to allow for the delocalization over three rings then there is sufficient driving force to planarize and delocalize charge over the entire chromophore.
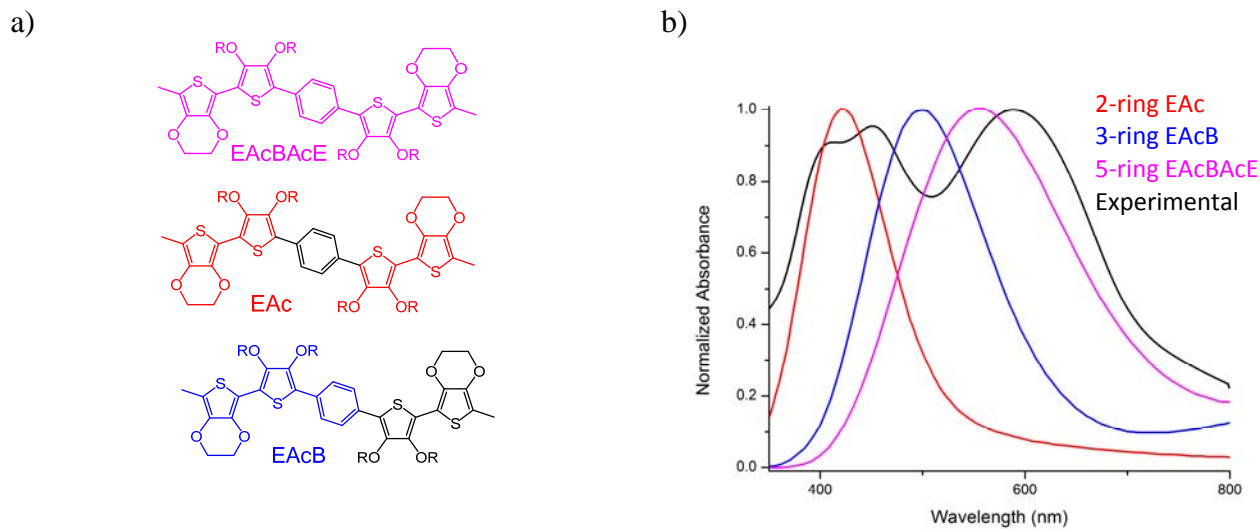
Figure 6 – (a) Structures indicating where the steric blocks in the structure may occur for limiting the radical cation delocalization (b) Calculated radical cation state absorptions of segmented portions of the EAcBAcE chromophore. (EDOT-AcDOT: blue, EDOT-AcDOT-DMOB: grey, EAcBAcE: red, experimental: black)

III.4 DFT/TDDFT Oligomeric Color Determination Study

Neutral Oligomer Color Study: In order to translate the predicted UV-Vis spectra into a perceivable color, L*, a*, and b* coordinates were determined using a Matlab script provided by the Reynolds group.[33] These coordinates can be thought of as a hemisphere centered on a 3-dimensional graph. Two axes, a* and b*, describe the amount of mixing and saturation between two colors which fall in a range from -100 to +100. The last axis, L*, indicates the brightness of these mixed colors in a range of 0 to 100.[34] A L* value of 100 is indicative of white and 0 is black. For the a* scale, -100 correlates to green while +100 is indicative of red. For b*, the negative limit corresponds to blue while the positive to yellow. A comparison between the experimental and DFT color coordinate data is summarized in Table 2. Both sets of numbers as well as the color swatches indicate a good correlation between the two sets of data. It can be seen in the cyan coordinates that there is excellent L* correspondence between experiment and theory, but a slight green shift in the a* value and yellow shift in the b*. The reason this occurs is explained through a close examination of the absorption minimum. In the simulated spectrum, the observed minimum appears at approximately 500 nm, which lies closer to the green region of the visible spectrum. However, the experimental minimum is found to occur closer to 450 nm, which is visibly more blue. For magenta, a green shift for the a* value and a blue shift for the b* coordinate produces an indigo color. Finally, the yellow polymer had a significant red shift in the a* value and slight blue shift in the b* coordinate, leading to an orange-gold color. The error in these modelled colorimetric values for magenta and yellow is again attributed to a Gaussian curve fit which produced peak broadening.[25] This broadening caused an excess absorbance of lower energy light for each simulation. Hence, ***color determination in the neutral state may be too subtle for this level of theory***.

	Cyan		Magenta		Yellow	
	Exp't	*DFT*	*Exp't*	*DFT*	*Exp't*	*DFT*
L*	71	74	53	46	96	86
a*	-34	-47	51	43	-7	17
b*	-21	-6	-41	-58	84	72
R	0	0	177	123	255	255
G	192	205	92	85	243	200
B	211	191	198	207	0	71

Table 2: Neutral color data in which the experimental and computational measurements are shown.

Oxidized Oligomer Color Study: By translating spectral data into colorimetric coordinates, further insight between the relationship of transmissivity and spectroscopic features is shown in Table 3. The computed L*a*b*/RGB values were nearly colorless and transparent whereas the experimental values retained blue and slightly grey hues. For all oligomers, the L* value from the DFT calculations is found to be 99, producing high transmissivity. When compared to experimental data, this value overstates the level of transparency each polymer would generate. This overstatement in transmissivity is again attributed to the Gaussian fit about the predicted excited states. A close examination of the experimental L* values indicated there is an increase in transmissivity going from cyan (86) to yellow (88) to magenta (91).   The DFT a* and b* values only deviate from experiment by ±2, indicating excellent color correlation. Overall, ***oxidized colorimetric data cannot be accurately produced using the DFT simulated spectra***.

	Cyan		Magenta		Yellow	
	Exp't	*DFT*	*Exp't*	*DFT*	*Exp't*	*DFT*
L*	86	99	91	99	88	99
a*	-3	-2	-2	-3	1	-2
b*	-3	-1	-4	-2	0	-1
R	206	247	221	244	223	247
G	217	253	231	254	220	253
B	221	254	237	255	221	254

Table 3: A table of bipolaron color data in which the experimental and computational measurements are shown.

IV. Personnel Supported with salary:

Principal Investigator:

     Aimée Tomlinson

Undergraduate Students:

     David Wheeler

     Lily Rainwater

     Alexa Green

     Melody Mullen

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1.

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Computationally Designed Oligomers for High Contrast Black Electrochromic Polymers

Grant/Contract Number
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Aimee Tomlinson

Program Officer
The AFOSR Program Officer currently assigned to the award

Kenneth Caster

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Abstract

The goal of this proposed effort is to use theoretical calculations to identify electrochromic materials that can be switched between 100% transmissive and tinted black states. This work was carried out as an active collaboration with the synthetic effort of the Reynolds group at Georgia Tech. We formed a tight feedback loop between our two groups, such that the computational effort narrowed down the promising oligomers which were then synthesized and characterized, then fed back to our group for continuous benchmarking. At the onset of our project, we were seeking CMY chromophores which when combined would give rise to a nearly black neutral state. Additionally, upon oxidation these polymers would have little to no tailing from the near IR thereby guaranteeing nearly a 100% transmissive material. These systems were given the title of cathodically coloring materials. After a set of structural experiments were performed a new type of system was found where we had a nearly transmissive neutral state and black oxidized state (anodically coloring materials). In all cases, we utilized a set of DFT/TDDFT treatments to produce insight of the impact structure-property relationships have on UV-Vis spectra. Our overall objective is to capitalize on our results to provide the Reynolds group with a set of oligomers that will produce the desired transmissive/black states.

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Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

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Appendix Documents

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